erthwrks

AIR EMISSIONS TESTING FOR INDUSTRY

Relative Accuracy Test Audit and Performance Testing

for

Air Products and Chemicals, Inc.

at the

Air Products Detroit Refinery in Detroit, MI

on the

Hydrogen Plant Heater
Unit: EU71-H2HTR-S3
Permit No. MI-ROP-A9831-2012c

Prepared for:

AIR PRODUCTS

Test Date: June 12, 2024
Erthwrks Project No. 9599

STAC STACK TESTING ACCREDITATION COUNCIL

ACCREDITED TO ASTM D7036 ONLY CERT #6147.01

Louisiana Environmental Lab Accreditation Program LELAP

CARB

Endorsement Page

This report was developed in accordance with the requirements designated in the applicable regulatory permit(s) and or regulatory rules. To the best of my knowledge the techniques, instrumentation, and calculations presented in this report will serve to accurately and efficiently detail the results of the test campaign requirements.

Erthwrks, Inc.

Name: Jason Dunn

Title: QA Specialist

Signature:

This report has been reviewed for accuracy and completeness. The actions presented in this report are, to the best of my knowledge, an accurate representation of the results and findings of the test campaign. Erthwrks, Inc. operates in conformance with the requirements on ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies and is accredited as such by the Stack Testing Accreditation Council (STAC) and the American Association for Laboratory Accreditation (A2LA).

Erthwrks, Inc.

Name: John Wood

Title: Technical Director

Signature:

Table of Contents

1.0 INTRODUCTION 4

1.1 Identification, location and dates of tests 4
1.2 Purpose of Testing 4
1.3 Description of Source 4
1.4 Contact Information 5

2.0 SUMMARY OF RESULTS 6

3.0 SOURCE DESCRIPTION 6

3.1 Description of the process 6
3.2 Applicable permit and source designation 7
3.3 Type and quantity of materials processed during tests 7

4.0 SAMPLING AND ANALYTICAL PROCEDURES 7

4.1 Gaseous Sampling – NOx, CO, CO_2, and O_2 7
4.2 Gaseous Emissions – VOC as THC (Method 25A) 8
4.3 Filterable Particulate Matter Sampling – EPA Method 5 9
4.4 EPA Method 202 – Condensable Particulate Matter 10
4.5 EPA Method CTM-013 (ALT-133 Analysis) H_2SO_4 Determination 11
4.6 RATA Procedures 12
4.7 Discussion of sampling procedure or operational variances 12

ATTACHMENTS

A. Detailed Results of Emissions Test
B. Quality Control Documentation
C. Example Calculations
D. Sampling Datasheets
E. Raw Datalog Records
F. Calibrations and Certifications
G. CEMS Logs and Operational Data
H. Laboratory Analysis

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the Hydrogen Plant Heater in operation at the Air Products Detroit Refinery, located in Detroit Michigan. The testing program was conducted on June 12, 2024.

1.2 Purpose of Testing

The exhaust from Hydrogen Plant Heater was sampled and analyzed to determine the relative accuracy of the associated carbon monoxide (CO) and oxides of nitrogen (NOx) continuous emissions monitoring system (CEMS) in accordance with the requirements in the Permit No. MI-ROP-A9831-2012c and the Title 40 CFR Part 60, Appendix F. In addition, compliance testing was conducted to determine the compliance status of the units' emission for filterable and condensable particulate matter (PM), sulfuric acid (H_2SO_4) and volatile organic compounds (VOCs).

1.3 Description of Source

Air Products and Chemicals, Inc. operates the Hydrogen Plant Heater designated as EU71-H2HTR-S3 in the refinery. This report addresses the RATA for the CEMS associated with the unit as well as the required compliance test for PM/PM_{10}, H_2SO_4 and VOC. Table 1.1 below details the CEMS analyzer information.

Table 1.1—Air Products Hydrogen Plant Heater CEMS Details

Hydrogen Plant Heater CEMS	Manufacturer	Model No.	S/N
NOx	Thermo	42i	1133550789
CO	Siemens Ultramat 6E	7MP2023	N1B3398

1.4 Contact Information

Air Products and Chemicals, Inc.
Steve Young
Site Manager
Detroit & Midwest SMART H2 Plants
Work: (313) 203-5153
Cell: (734) 757-7039
youngsr1@airproducts.com

Erthwrks, Inc.
Mike Oleszko
Project Manager
P.O. Box 150549
Austin, TX 78745
737-354-8999 office
888-573-9994 fax
moleszko@erthwrks.com

Erthwrks, Inc.
John Wood
Technical Director
P.O. Box 150549
Austin, TX 78745
512-585-1685 office
888-573-9994 fax
jwood@erthwrks.com

Erthwrks, Inc.
Jason Dunn
QC Specialist
P.O. Box 150549
Austin, TX 78745
614-565-9177 office
888-573-9994 fax
jdunn@erthwrks.com

Facility Location:
Air Products and Chemicals, Inc.
Detroit Hydrogen Plant
1300 South Fort Street
Detroit, MI 48217

2.0 SUMMARY OF RESULTS

Table 2.1—Air Products Hydrogen Plant Heater (EU71-H2HTR-S3) CEMS RATA Results

Pollutant Measured	Performance Specification	Relative Accuracy	Applicable Limit	Pass/Fail
NOx (ppm @ 0% O_2)	Performance Spec. 2	1.0% RA_{AS}	$10\%_{AS}$	***Pass***
NOx (lb/MMBtu)	Performance Spec. 2	3.7% RA_{AS}	$10\%_{AS}$	***Pass***
CO (lb/hr)	Performance Spec. 6	2.7% RA_{AS}	$5\%_{AS}$	***Pass***

Table 2.2—Air Products Hydrogen Plant Heater (EU71-H2HTR-S3) Compliance Test Results

Pollutant Measured	Methodology	Measured Results	Applicable Limit	Pass/Fail
NOx	EPA Method 7E	0.005 lb/MMBtu	0.013 lb/MMBtu	***Pass***
CO	EPA Method 10	1.1 tons/yr	13 tons/yr	***Pass***
PM	EPA Method 5	0.0003 lb/MMBtu	0.0034 lb/MMBtu	***Pass***
PM_{10}	EPA Method 5/202	0.0042 lb/MMBtu	0.010 lb/MMBtu	***Pass***
VOC	EPA Method 25A/4	0.0012 lb/MMBtu	0.0055 lb/MMBtu	***Pass***
H_2SO_4	EPA Method CTM-013	0.43 ppm	n/a	***n/a***

3.0 SOURCE DESCRIPTION

3.1 Description of the process

Air Products owns and operates the Detroit Hydrogen Plant located within the Marathon Detroit Refinery. The Hydrogen Plant supplies hydrogen (H_2) to the Detroit Hydrogen Plant, which is utilized in the petroleum refining process. Natural gas, refinery fuel gas, and/or a high-pentane (C5H12) refinery steam are converted into 99.9% pure H_2 and high-pressure steam using steam/methane reforming technology. The unit consists of process vessels, a heater, compressors, pumps, piping, drains and other various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Hydrogen Plant Heater (EU71-H2HTR-S3) is fired by a combination of refinery gas, pressure swing absorption gas, syngas and/or natural gas. The heater is equipped with an SCR system to control emissions, which are vented to the atmosphere via the Hydrogen Plant Heater Stack (SV71-H2HTR).

3.2 Applicable permit and source designation

Air Products and Chemicals, Inc. operates the Hydrogen Plant Heater (EU71-H2HTR-S3) under EGLE Renewable Operating Permit No. MI-ROP-A9831-2012c and is required to conduct an annual RATA to demonstrate the relative accuracy of the CEMS associated with this unit and to periodically determine the H_2SO_4 and VOC exhaust emissions.

3.3 Type and quantity of materials processed during tests

During the emission testing on June 12, 2024, the Hydrogen Plant Heater was tested while operating at the maximum achievable load condition. **NOTE:** For this testing program, the average H_2 production was approximately 55.1 mmscf/day and the average unit firing rate was 466.5 MMBtu/hr. This operational data was provided by the facility and is located in Attachment F of this report.

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 Gaseous Sampling – NOx, CO, CO_2, and O_2

For the gaseous sampling, Erthwrks utilized a stainless-steel probe, of sufficient length to reach all sampling points, inserted into a sampling port that is located on the stack in accordance with EPA Method 1. The sample is extracted through the probe, a heated Teflon sampling line, to a heating filter. The sample then enters a minimum contact sample conditioner that cools and removes moisture from the gas matrix prior to entering the Erthwrks sampling manifold.

Erthwrks followed all quality assurance and quality control procedures as defined in US EPA 40 CFR 60 Appendix A. The Calibration Error (CE) Test was conducted as specified in EPA Method 7E §8.2.3. In accordance with this requirement, a three-point analyzer calibration error test was conducted prior to sampling. The CE test was conducted by introducing the low, mid, and high-level calibration gasses (as defined in EPA Method 7E §3.3.1-3) sequentially and the response was recorded. The results of the CE test are acceptable if the calculated calibration error is within ±2.0% of calibration span (or ≤ 0.5 ppmv).

The Initial System Bias and System Calibration Error Check was conducted in accordance with EPA Method 7E §8.2.5. The upscale calibration gas was introduced at the probe upstream of all sample system components and the response recorded. The procedure was repeated with the low-level gas and the response recorded. During this activity, the sample system response time was also recorded. This specification is acceptable if the calculated values of the system calibration error check are within ±5.0% of the calibration span value (or ≤0.5 ppmv).

After each test run, the sample system bias check is conducted to validate the run data. The low-level and upscale drift are calculated using Equation 7E-4. The run data is valid if the calculated drift is within ±3.0% of the calibration span value (or ≤0.5 ppmv).

After each test run, the corrected effluent gas concentration was calculated as specified in EPA Method 7E §12.6. The arithmetic average of all valid concentration values are adjusted for bias using equation 7E-5B.

4.2 Gaseous Emissions – VOC as THC (Method 25A)

The determination of the VOC as total hydrocarbon compounds (THC) concentration followed all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A. The calibration error (CE) test was conducted following the procedures specified in EPA Method 25A §8.4. In accordance with this requirement, a four-point analyzer calibration error test was conducted prior to exhaust sampling. This CE test was conducted by introducing the zero, low, mid, and high-level calibration gases (as defined by EPA Method 25A §7.1.2-5) and the responses recorded. The results of the CE test are acceptable if the results for the low and mid-level calibration gasses are within ±5.0% of the predicted responses as defined by the linear curve from the zero and high-level results. During this activity, the sample system response time was also recorded in accordance with EPA Method 25A §8.5.

Immediately following the completion of each test run, the drift determination was conducted to validate the test data in accordance with EPA Method 25A §8.6.2. The test data is valid if the calculated drift is within ±3.0% of the span value (EPA Method 25A §13.1.2). In addition, at the request from EGLE, the THC raw data is corrected for analyzer drift using EPA Method 7E Equation 7E-B5. The THC is measured on a wet basis and is converted to a dry basis using moisture data from a Method 4 or Method 5 sampling train.

Because the THC concentration was found to be below the permitted limit for VOC, the test results are reported as VOC (as THC) and therefore no Method 18 analysis was required to subtract methane and ethane from the THC results.

The figure below details the Erthwrks Gaseous Sampling System.

Figure 1: Example Erthwrks Gaseous Sampling System Diagram

4.3 Filterable Particulate Matter Sampling – EPA Method 5

EPA Test Method 1 was used for the selection of sampling points. Stack dimensions, number of sample ports and sample port locations were confirmed prior to testing to determine the appropriate number of traverse points for the test.

EPA Test Method 5 was used to determine filterable particulate matter emission rates. Method 5 is the method at which particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter and on the lining of the isokinetic probe maintained at a temperature of 120 ± 14°C. Upon completion of each test run, the nozzle and probe liner were rinsed and brushed with acetone. The acetone rinse catch was collected and combined with the filter holder rinse and labeled as "front half rinse". The total PM mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically. Filterable PM was calculated by combining the net gravimetric gain of the filter and the net gravimetric gain of the evaporated front half rinse. Figure 2 below shows the Method 5 sampling system components.

Figure 2: Example Particulate Matter Sampling Train

4.4 EPA Method 202 – Condensable Particulate Matter

For the determination of PM/PM_{10}, CPM was measured via EPA Method 202. The Method 202 components begin at the back half of the Method 5 filter housing. The filterable particulate matter is removed in these "front half" components. The condensable particulate matter is then collected by drawing the filtered gas through a water jacketed, spiral condenser maintained at $65^{o} – 85^{o}$ F. The cooled effluent gas is then passed through two empty impingers and finally through a hexane extracted Teflon filter. Upon completion of each test run, the moisture collected in this portion of the sampling train is purged with ultra-high purity (UHP) nitrogen gas for one hour to remove any dissolved sulfur dioxide. The moisture is collected in a container and combined with the deionized water used to rinse all Method 202 sampling glassware two times.

The glassware is next rinsed with Hexane and acetone. These rinses are collected and combined in an additional container. The Teflon filter is removed from the filter housing, labeled, and collected. Gravimetric analysis is then conducted on the extracted, evaporated samples for each run.

4.5 EPA Method CTM-013 (ALT-133 Analysis) H_2SO_4 Determination

The H_2SO_4 emissions were determined utilizing the conditional test method 13 (CTM-013). The sample was extracted at a constant rate through a quartz lined heated probe (>350 ˚F), A heated quartz filter holder and filter (>500 ˚F), and through a Modified Grahm condenser (H_2SO_4 Condenser) with Type C glass frit and 200 cm of 5-mmID glass tubing condenser coil. The H_2SO_4 condenser is maintained between 167 to 185 ˚F. Because SO_2 was not to be determined via this method, the sample was then passed through four impingers with the specifications delineated in EPA Method 4.

The sampling was conducted at a single point at a constant rate of about 10 L/min and the DGM readings and all temperatures were recorded every five minutes. After the completion of the test run, the samples were recovered in accordance with the test method and the samples were sent to Enthalpy Analytical for analysis via Ion Chromatography (ALT-133).

See the figure below that details the CTM-013 Sampling Train.

Figure 3: Example Erthwrks H_2SO_4 System Diagram

4.6 RATA Procedures

The RATA testing was conducted following the sampling and measurement procedures found in the EPA Part 60, Appendix B, Performance Specifications which requires that EPA Reference Methods, from EPA Part 60, Appendix A, be utilized to conduct independent stack emissions measurements for comparison with installed CEMS readings. The following performance specifications will be used during this testing program.

- EPA Performance Specification 2 for NOx relative accuracy
- EPA Performance Specification 6 for CO relative accuracy

As required by these methods, the use EPA Protocol 1 gases are mandatory and were used for this portion of the project.

A minimum of nine (9) RATA test runs were conducted at each exhaust stack for a minimum duration of twenty-one (21) minutes for each run. A 3-point traverse located at 16.7%, 50.0%, and 83.3% of the way across the stack (or 0.4, 1.2, and 2.0 meters from the stack wall) was conducted during each RATA test run (7 minutes per point). A maximum of twelve (12) RATA test runs will be conducted and up to three test runs may be discarded and not used to determine relative accuracy. The results of the reference method tests were compared to CEMS measurement data from the same time periods to determine the relative accuracy of the CEMS.

For NOx, the results of the RATA test are considered acceptable if the calculated relative accuracy does not exceed 20.0% as calculated by Equation 2-6 in Performance Specification 2. Alternatively, for affected units where the average of the reference method measurements is less than 50 percent of the emission standard (emission limit), the relative accuracy must not exceed 10% when the applicable emission standard is used in the denominator of Eq. 2-6.

For the CO CERMS RATA, a complete flow and temperature traverse was performed for each RATA run, with the first three RATA runs coincided with the three PM test runs. For the following six runs a single moisture for each series of three RATA runs (three flow traverses. The reference method CO concentration and flowrate data was used to calculate the CO in units of lbs/hr and compared to the CERMS lb/hr data. The results of the RATA test is considered acceptable if the calculated relative accuracy does not exceed 20.0% as calculated by Equation 2-6 in Performance Specification 2. Alternatively, for affected units where the average of the reference method measurements is less than 50 percent of the emission standard (emission limit), the relative accuracy must not exceed 10% when the applicable emission standard is used in the denominator of Eq. 2-6.

4.7 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted the emissions testing with no sampling or procedural variances.